Mechano-chemical syntheses, crystal structures and photo-luminescent properties of a new hydrazone and its nickel and cadmium complexes

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Abstract

A new hydrazone, *Z*-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate($C_9H_{11}N_3O_2$; Hpyec) and its metal complexes bis(*Z*-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate) nickel(II) monohydrate, $[Ni(pyec)_2]\cdot H_2O$ (**1**) and bis(acetato)(*Z*-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate) cadmium (II), $[Cd(Hpyec)(CH_3COO)_2]$(**2**), have been prepared by mechano-chemical syntheses and characterized by elemental analysis, UV-visible, IR and NMR spectroscopy, TG-DTA, and solid state emission techniques. The X-ray single crystal structures of both complexes were determined: in **1**, the Ni^{2+}ion is coordinated by two N, N, O-tridentate anionic ligands to generate a distorted *cis*-NiO_2N_4 octahedron. In **2**, the cadmium atom is seven-coordinated by one neutral N,N.O-tridentate ligand and two chelating acetate ions to generate a very-distorted CdN_2O_5 pentagonal bipyramid with the Hpyec atoms occupying both axial and one equatorial site. Crystal data: **1**, $C_{18}H_{22}N_6NiO_5$, M_r = 461.12, monoclinic, $P2_1/c$, a = 10.8759 (3) Å, b = 11.7055 (4) Å, c = 16.8424 (5) Å, β = 108.583 (1)°, V = 2032.38 (11) Å^3, Z = 4, $R(F)$ = 0.023, $wR(F^2)$ = 0.065;**2**, $C_{13}H_{17}CdN_3O_6$, M_r = 423.69, monoclinic, Cc, a = 13.0215 (10) Å, b = 15.8104 (11) Å, c = 7.99 (6) Å, β = 96.692 (2)°, V = 1621.7 (2) Å^3, Z = 4, $R(F)$ = 0.017, $wR(F^2)$ = 0.038.

Key words: Green synthesis; hydrazone; metal complexes; crystal structures; emission study

Introduction

Hydrazone derivatives, containing an R,R′C=N–NHR′′ (R, R′, R′′ = H, alkyl, aryl) grouping, represent an extensive family of Schiff-base compounds and have been extensively studied because of their potential applications as anticancer, antiviral, antibacterial and antifungal agents [**1–5**]. In terms of coordination chemistry, the azomethine N atom of hydrazone derivatives is known to exhibit strong donor behavior towards transition metal ions [**6**]. The introduction of additional donors like carbonyl oxygen atoms (*i.e.*: R,R′C=N–NH**CO**R′′) provides the possibility for different coordination modes for hydrazones resulting in structural variety in their metal complexes [**7–9**]. Aroylhydrazone complexes of transition metal ions are known to provide useful models for elucidating the mechanism of enzyme inhibition by hydrazine derivatives [**10**]. Many potential hydrazone ligands have been synthesized using heteroaromatic carbonyl compounds in combination with different hydrazine derivatives [**11–13**]. Recently, hydrazones derived from 2-pyridine carboxaldehyde have been used to synthesize many biologically active metal complexes [**14–19**].

Though many hydrazine derivatives have been used to synthesize hydrazone ligands, ethyl carbazate ($NH_2NHCO_2CH_2CH_3$), the acyl hydrazine derivative, has been less explored [**20–22**]. To the best of our knowledge, there are no previous reports on metal complexes of the hydrazone derived from the combination of 2-pyridine carboxaldehyde and ethyl carbazate. Ethyl carbazate itself is an important raw material and intermediate, which has been widely used in the syntheses of medicines, herbicides, plant growth regulators, germicides and insecticides [**23**]. Recently we have explored the ligating property of ethyl carbazate by synthesizing a series of metal complexes with different structural topologies [**24–26**].

In terms of synthesis, mechanochemistry has been shown [**27**] to be a powerful alternative to the conventional solution-based method: its potential advantage includes milder reaction conditions, fewer byproducts, shorter reaction times and high yields. This method has been employed to synthesize a variety of materials including coordination complexes having biological significance [**28–31**].

In this work we set out to investigate the following:

- The applicability of solvent-free mechano-chemical synthesis to prepare hydrazone carboxylates and their metal complexes;
- The coordination behaviour of the new ligand *Z*-ethyl 2-(pyridine-2yl methylene) hydrazone carboxylate, $C_9H_{11}N_3O_2$ (Hpyec) with different metal ions;
- The crystal structures, thermal and luminescence properties of these complexes.

Experimental

General

Ethylcarbazate and pyridine-2-carbaldehyde were purchased from Sigma-Aldrich. The metal salts and ethanol were purchased from Merck. All chemicals were used as received. Double distilled water was used for the recrystallization experiments. UV–Vis spectra for the complexes were recorded on a SHIMADZU UV–Vis spectrophotometer (UV-2450) using DMSO as solvent. A Perkin Elmer Spectrum-1spectrophotometer was used to record the IR-spectra (4000–450 cm^{-1}) using KBr pellets. The C, H and N contents were determined using an Elemental Vario EL II elemental analyzer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 500-MHz spectrometer in DMSO-d6 and D_2O. Photoluminescence spectra were recorded on Jobin-

Yvon Fluorolog-2-11 spectroflurimeter. The simultaneous TG-DSC measurements were carried out using a Netzsch STA449F3 Jupiter thermal analyzer under a nitrogen atmosphere. Mass spectra were recorded on a JEOL GCMATE II GC-MS mass spectrometer.

Synthesis of Z-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate (Hpyec)

The Hpyec ligand was prepared using solvent-free conditions: ethylhydrazinecarboxylate and pyridine-2-carbaldehyde were mixed in a 1:1 mole ratio and the slurry was ground for 10 minutes using a mortar and pestle. A colorless powder was formed, which was washed with water and air dried. The purity of the compound was checked by TLC. Yield: 61.6% (0.585 g); m.p. 119 ℃.*Anal*. Calcd. For $C_9H_{11}N_3O_2$(%): C 55.95; H 5.70; N 21.76. Found: C 54.47; H 5.63; N 20.84. Selected IR bands (KBr pellet, cm^{-1}): 3173(N–H), 1749(C=O), 1587(C=N),1228(C–O), 1047(N–N). UV-Vis (DMSO), λ_{max} (nm): 290. ^{1}H-NMR(δ ppm), (DMSO-d6); t, 1.24(C**H**$_3$–CH_2–O–); q, 4.27(CH_3–C**H**$_2$–); s, 9.76(C**H**=N–); s, 8.55(=N–C**H**); m, 7.22–8.11 (Ar-ring).^{13}C-NMR (δ ppm), (DMSO-d6); 14.61, 40.96, 62.19, 120.89, 124.10, 136.60, 144.74, 149.62, 153.21.

Synthesis of bis(Z-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate) nickel(II) monohydrate (1) and bis(acetato)(Z-ethyl 2-(pyridine-2yl-methylene) hydrazine carboxylate) cadmium(II) (2)

To prepare the metal complexes, 1.00 mmol of the appropriate acetate salt, $Ni(CH_3COO)_2{\cdot}4H_2O$, (0.248 g) or $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.267 g) was mixed with 1.00 mmol of the Hpyec (0.193 g) ligand. The solid mixture was ground for 45 minutes using a mortar and pestle. The nickel reaction resulted in a dark green powder and the cadmium powder was colorless. Compound **1** is

soluble in ethanol so was washed with water, whereas compound **2** is soluble in water and was washed with ethanol. Single crystals of **1** and **2** suitable for X-ray diffraction were obtained by recrystallizing the compounds from the mixed solvents of water and ethanol (1:1 *v*/*v*). The recrystallised products and the as-synthesised powders have the same composition as shown by elemental analysis. **1**: yield 84.6% (0.373 g); *Anal*. Calcd. For $C_{18}H_{22}N_6NiO_5$(%): C46.84; H4.77; N18.22. Found: C 46.65; H 4.81; N 18.16. Selected IR (KBr pellet, cm^{-1}): 1519(C=N), 1291(C–O), 1059(N–N). UV-Vis (DMSO), λ_{max} (nm): 289, 371, d–d band at 857. **2**: yield 76.5% (0.352 g); *Anal*. Calcd. For $C_{13}H_{17}CdN_3O_6$(%): C 36.82; H 4.01; N 9.91. Found: C 36.68; H 4.37; N 10.18. Selected IR (KBr pellet, cm^{-1}): 3132(N–H), 1686(C=O), 1559(C=N), 1286(C–O), 1056(N–N). UV-Vis (DMSO), λ_{max} (nm): 291 and 373. ^{1}H-NMR (δ ppm), (D_2O); s, 1.84($C\mathbf{H_3}COO^-$); t, 1.92($H_3C\mathbf{CH_2}O$-); q, 4.23($H_3C\mathbf{CH_2}O$-); m, 7.53-8.47(Ar-ring). ^{13}C-NMR (δ, ppm), (D_2O); 13.59, 22.05, 64.07, 127.18, 140.59, 146.80, 149.79, 157.24, 181.61.

Crystal structure determinations

The intensity data were collected using a Bruker APEX IICCD diffractometer [32] using Mo Kα radiation, λ = 0.71073 Å (*T* = 20 °C). For **1**, a dark green block of dimensions 0.30 × 0.25 × 0.20 mm was chosen for data collection and for **2**, a colorless block, 0.20 × 0.20 × 0.15 mm, was used. Empirical (multi-scan) absorption corrections were applied with SADABS [33] at the data-reduction stage. Both structures were solved without difficulty by direct methods using SHELXS-97 [34] and the atomic models were developed and refined against $|F|^2$ with SHELXL-2014 [**35**]. The O-bonded H atoms for **1** and the N-bonded H atom for **2** were found in difference maps and their positions were freely refined. The C-bonded H atoms were geometrically placed and modelled as riding atoms with C–H = 0.93–0.97 Å. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The constraint U_{iso}(H) =

1.2U_{eq}(carrier) or 1.5U_{eq}(methyl C) was applied in all cases. The structures were analysed and verified with PLATON [**36**] and the molecular graphics were generated with ORTEP-3 [**37**]. Crystal data are summarized in Table 1 and full details are available as supplementary material (cif format).

Results and discussion

Infrared spectra

The IR spectrum of the free ligand shows absorptions at 1749, 1587 and 3172 cm^{-1}due to the –CONH– (amide-I), –CH=N and –NH stretching vibrations, respectively. In the spectrum of **1**, the –NH and carbonyl peak have disappeared and a new peak around 1291 cm^{-1}, which can be assigned to a –C–O stretch, is present. This suggests that the ligand is deprotonated and coordinated as an enolate anion. In the IR spectrum of **2**, however, the carbonyl stretch is observed with a diminished absorption frequency of 1686 cm^{-1}. Also, in the spectrum of both complexes, the absorption frequency due to the azomethine group is lowered (1519 cm^{-1} for **1** and 1559 cm^{-1} for **2**) compared to the free ligand (1587 cm^{-1}). The IR spectra therefore suggest that in compound **1**, the ligand is coordinated to metal through its azomethine N atom and deprotonated O atom whereas in **2** it is coordinated *via* the azomethine N and carbonyl O atoms. Further, a peak around 622 cm^{-1} in the spectrum of the ligand is assigned to the pyridine ring deformation (in-plane) and it is increased in value in the spectra of metal complexes (682 cm^{-1} for **1** and 677 cm^{-1} for **2**). This is an indication of coordination of the pyridine N atom to the metal ion in both complexes. Further, in the spectrum of **2**, broad absorptions around 1559, which is likely to be the overlapped peaks of azomethine and carboxylate group and 1422 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of acetate anions,

respectively. The small difference ($\Delta\upsilon$=138 cm^{-1}) indicates that the acetate ligand exhibits an O,O-chelating mode [**38**]. In the spectrum of **1**, a broad peak around 3420 cm^{-1} is assigned to O–H stretches of the water molecule of crystallization. All these observations are confirmed by the crystal structure determinations (*vide infra*).

Crystal structure of 1

The molecular structure of **1** (Fig. 1) consists of octahedral, monomeric, neutral complexes in which the nickel atom is bonded to a pair of deprotonated anionic hydrazone ligands. Each ligand chelates through its pyridine and azomethine nitrogen atoms and its carbonyl oxygen atom to generate a moderately distorted *cis*-NiN_4O_2 octahedral donor set (Table 1), in which the *cis*-bond angles vary from 75.66 (4) to 95.68 (5)°. The charge-assisted Ni–N_a (a = azomethine) bond lengths are notably shorter than the Ni–N_p (p = pyridine) links. Within the C1 ligand, the key bond lengths in the hydrazone fragment are C6–N2 = 1.286 (2) Å, N2–N3 = 1.3559 (18) Å and C7–N3 = 1.345 (2) Å; comparable values for the C10 ligand are C15–N5 = 1.284 (2) Å, N5–N6 = 1.3631 (17) Å and C16–N6 = 1.3423 (19) Å. The N–N bond lengths are notably shorter than nominal N–N single bonds (~1.41 Å), indicating significant electronic delocalization between the C=N and ester groups. Both ligands are approximately planar: the dihedral angles between the pyridine ring and hydrazone grouping are 1.37 (5)° and 5.21 (5)° for the C1 and C10 ligands, respectively. The ethyl side chains adopt extended conformations [C7–O2–C8–C9 = –173.89 (16)° and C16–O4–C17–C18 = 155.70 (18)°] in both ligands.

The tridentate $C_9H_{10}N_3O_2^-$ligands each generate two five membered chelate rings with the following bite angles: N1–Ni1–N2 = 78.65 (5)°, N2–Ni1–O1 = 75.78 (5)°, N4–Ni1–N5 = 78.71 (5)° and N5–Ni1–O3 = 75.66 (4)°. For the N1 ligand, both chelate rings are almost planar (r.m.s.

deviation for the C6 and N3 rings = 0.003 and 0.018 Å, respectively). For the N4 ligand, the chelate ring including N6 is almost planar (r.m.s. deviation = 0.028 Å) but the C15 ring is better described as a shallow envelope with the metal atom deviating from the other atoms (r.m.s. deviation = 0.006 Å) by –0.2082 (19) Å. The dihedral angled between the pyridine–hydrazone–carboxylate fragments of the ligands is 85.437 (16)°.

The extended structure of **1** features O–H…N hydrogen bonds arising from the water molecule of crystallization, which link the complex molecules into [100] chains (Fig. 2) of alternating $Ni(pyec)_2$ molecules and water molecules: adjacent molecules in the chain are related by translational symmetry. Some weak C–H…O interactions are also observed (Table 2).

Crystal structure of 2

The asymmetric unit of **2** (Fig. 3) consists of a single molecule in which the neutral Hpyec ligand shows the same N, N, O-tridentate bonding mode as in **1**. The cadmium coordination is completed by two chelating acetate ions (Table 3) and the resulting CdN_2O_5 polyhedron (Fig. 4) can be just be described as an extremely distorted pentagonal bipyramid. The Hpyec atoms occupy both the nominal axial [N1–Cd1–O1 = 136.19 (12)°] positions and one equatorial site and the acetate anions occupy the remaining equatorial sites: the O3–Cd1–O4 and O5–Cd1–O6 bite angles of 53.57 (14)° and 53.59 (15)°, respectively, are far smaller than the other equatorial angles. It is notable that the $Cd–O_a$ (a = acetate) bond lengths show significant asymmetry [δ = 0.227 (8) Å for the C10 anion and 0.163 (8) for the C12 anion] although the acetate C–O bond lengths are almost the same for both anions. Within the Hpyec ligand in **2**, key bond distances are C6–N2 = 1.264 (5) Å, N2–N3 = 1.354 (4) Å and C7–N3 = 1.356 (5) Å: these data barely differ from the corresponding values for **1**, suggesting that deprotonation has little effect on the electronic structure of the ligand.

The bite angles of the Hpyec ligand to the cadmium atom in **2**[N1–Cd1–N2 = 69.33 (12)° and N2–Cd1–O1 = 66.90 (11)°] are notably smaller than the equivalent values for **1**, which may correlate with the larger size of Cd^{2+} compared to Ni^{2+}. Both chelate rings in **2** are almost planar (r.m.s. deviations for the C6 and N3 rings = 0.009 Å and 0.010 Å, respectively) and the complete ligand is close to planar (r.m.s. deviation for the 14 non-hydrogen atoms = 0.010 Å). The dihedral angles between the C1–C7/N1–N3/O1/O2 fragment of the ligand and the C10 and C12 acetate planes are 89.15 (16)° and 89.88 (18)°, respectively; the dihedral angle between the acetate planes is 12.0 (4)°. The metal atom deviates from the C10 and C12 acetate planes by 0.010 (9) and 0.086 (11) Å, respectively. In the crystal of **2**, N–H…O hydrogen bonds link the molecules into [001] chains, with adjacent molecules in the chain related by *c*-glide symmetry; the acceptor O atom is part of an acetate group (Fig. 5). The packing is consolidated by weak C–HΛO links.

Related structures

There are no structures containing a 2-py–CH=N–N(H)–CO_2R grouping bonded to nickel or cadmium in the Cambridge Structural Database (updated to April 2017) but 16 and 15 ‘hits’ respectively were recorded for a 2-py–CH=N–N(H)–COR(R = C, N) grouping bounded to Ni^{2+} or Cd^{2+}, all of which show N,N,O-tridentate bonding of the ligand to the metal ion.

Thermal behavior

The DSC curve of the free ligand shows an endothermic peak around 132°C without any weight loss, which is attributed to the melting of the ligand. The TG curve further shows that the ligand is stable up to 240 °Cafter which it decomposes completely by around 400°C. An exothermic

peak is observed for this step of decomposition in DSC trace. Compound **1** and **2** are stable up to 160 °C and 210 °C, respectively. The thermogram for **1** shows two distinct weight losses below 400 °C. The first step is due to the loss of the water molecule of crystallization (calc. 3.9%; obs. 4.7%) between 160–195 °C, which is a typical temperature for such a process [**39, 40**]. The anhydrous intermediate is stable up to 240 °C, after which it decomposes to give $NiCO_3$ (calc. 74.2%; obs. 71.1%) as the final product (600 °C). Compound **2** decomposes continuously from 210–800 °C without any distinct intermediates to result in CdO (calc.; 69.7%, obs.; 70%) as the end residue. All decomposition steps for both the compounds are endothermic in nature as shown by DTA.

Photoluminescence study

The photoluminescence spectra of the free ligand and metal complexes were recorded in the solid state (λ_{ex} = 300 nm) (Fig. 6). The free ligand shows two intense bands at 355 and 401 nm and weak bands at 467 and 527 nm. The multiple emission bands may be due to the presence of more than one different chromophore [**41**]. The nickel and cadmium complexes emit at 396 and 401 nm, respectively. The reduced intensity of these bands compared to the free ligand may be due the increase of the rigidity of the ligand on coordination [**42**]. Since the emission pattern and the peak positions of the metal complexes are very similar to that of the free ligand, the photoluminescence property of the metal complexes can be assigned as being due to intra-ligand transitions.

Conclusions

In this work, a new unsymmetrical hydrazone, derived from 2-pyridine carboxaldehyde and ethyl carbazate and its nickel and cadmium complexes have been synthesized by using a 'green' mechano-chemical synthesis. The crystal structures revealed octahedral and pentagonal bipyramidal coordination geometries for nickel and cadmium, respectively. The coordination mode of the hydrazone is N, N, O-tridendate in both complexes, but it is coordinated in the deprotonated enolic form in the case of nickel whereas it is coordinated as a neutral ligand to cadmium. The nickel and cadmium compounds are thermally stable up to 160 and 210° C, respectively. The hydrazone and the metal complexes exhibit photoluminescence, which may be ascribed to intra-ligand transitions in all cases.

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FIGURE CAPTIONS

Fig 1: The molecular structure of **1** showing 50% displacement ellipsoids.

Fig 2: Fragment of a [100] hydrogen-bonded chain in the crystal of **1**. Symmetry code: (i) *x*–1, *y*, *z*.

Fig 3: The molecular structure of **2** showing 50% displacement ellipsoids.

Fig 4. A view of the distorted pentagonal bipyramidalCdN_2O_5coordination polyhedron in **2**

Fig 5: Fragment of an [001] hydrogen-bonded chain in the crystal of **2**. Symmetry code: (i) *x*, –*y*, *z*–½.

Fig. 6: Photoluminescence spectra of Hpyec, **1** and **2**